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Specification

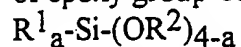
1. Title of Invention

Composite body which has cured coat

2. Claims

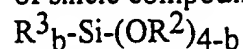
Composite body which has cured coat which is obtained by coating and curing the mixture which contains at least the following (A), (B), and (C).

(A) Hydrolyzate which is obtained by adding hydrochloric acid solution to at least one kind of epoxy group-containing silicic compound expressed by the general formula (1)



(In the formula, R^1 is an epoxy group-containing organic group, R^2 is an alkyl group of carbon number 1 ~ 5, and a is 1 ~ 3).

(B) Hydrolyzate which is obtained by adding hydrochloric acid solution to at least one kind of silicic compound expressed by the general formula (2)



(In the formula, R^3 is an alkyl group of carbon number 1 ~ 6, vinyl group, methacryloxy group, mercapto group, or chlorine-containing organic group, and b is 0 ~ 3).

(C) $SnCl_2$

3. Detailed Description of the Invention

The present invention relates to a composite body which is a plastic product, a wooden product, a metal product, etc. which is covered with cured coat in order to improve the surface hardness, wear resistance, chemical durability, corrosion resistance, light resistance, etc..

For example, although plastic moldings, in particular, of polycarbonate base resin, acrylic resin, styrene resin, vinyl chloride resin, etc. are excellent in transparency, light weight, workability, shock resistance, etc., they have such faults as low wear resistance, low chemical durability, and they are particularly vulnerable to solvent.

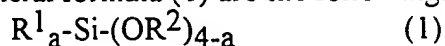
In order to remedy these faults, many methods have been proposed to cover them with thermosetting coat, but any of them are not satisfactory enough. For example, a

combination of organoalkoxysilane, teteraalkoxysilane, etc., or further their mixtures with various resins have been known, but none of them is good in all of wear resistance, hot water durability, high density, adhesion, pot life of the treating liquid, etc.. The cause of this is in the catalyst and/or the crosslinking agent. The catalyst and/or the crosslinking agent proposed in the past are as the following. Namely, they are hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, formic acid, sulfonic acid, paratoluenesulfonic acid, boron trifluoride, and their complex, Lewis acid such as SnCl_4 , ZnCl_2 , FeCl_3 , AlCl_3 , SbCl_3 , TiCl_4 , etc. and their complex, metal salt of organic acid such as sodium formate, zinc naphthenate, tin octylate, etc., perchloric acid, ammonium perchlorate, ammonium nitrite, borides, fluoroborides, alkalis such as sodium hydroxide, etc., polyhydric carboxylic acids, organometallic alcoholate such as tetrabutoxytitanium, etc., complex of organometallic compound such as metal acetylacetonate such as titanium acetylacetonate, aluminum acetylacetonate, etc., amines such as n-butylamine, guanidine, imidazole, amino group-containing silicic compound, etc., but all of them have various faults. Namely, hydrochloric acid, nitric acid, formic acid, sulfonic acid, paratoluenesulfonic acid, alkalis, ZnCl_2 , FeCl_3 , AlCl_3 , SbCl_3 , and organometallic salts are not practical since the hardness of the cured coat obtained is not enough. Also, amines are not practical since they require high temperature for satisfactory curing which tends to cause discoloration of the cured coat, and further, the pot life of the treating liquid is extremely short. When polyhydric carboxylic acid, boride, fluoroboride, or boron trifluoride is used, the hot water durability of the cured coat is not enough and its hardness is degraded by soaking in hot water, and thus it is not practical. The pot life of the treating liquid with organometallic alcoholate is short, and also, the complex of organometallic compound requires even higher temperature than amines for satisfactory curing, and thus these are not practical. Perchloric acid and its salt, ammonium perchlorate, etc. discolor the cured coat, and also the pot life of the treating liquid with them is short, and thus they are not practical. Relatively good results could be obtained with SnCl_4 and TiCl_4 , and the quality of the cured coat obtained is good, but the pot life of the treating liquid is short, and thus they are not practical.

The present inventors found that the combination of hydrochloric acid and SnCl_2 is the best as the catalyst and/or crosslinking agent which remedies the aforesaid faults, and gives cured coat which is excellent in surface hardness, wear resistance, chemical durability, corrosion resistance, light resistance, etc., and good in adhesion to the substrate material to be coated, and shows extremely superior performance in hot water durability, and yet the pot life of the treating liquid is long, and also, the curing can be completed at relatively low temperature in a short time.

Namely, the present invention is a composite body which has cured coat of the mixture which is featured in that it at least contains the hydrolyzate which is obtained by hydrolyzing the epoxy group-containing silicic compound expressed by the general formula (1) by aqueous solution of hydrochloric acid, and hydrolyzate which is obtained by hydrolyzing the silicic compound expressed by the general formula (2) by aqueous solution of hydrochloric acid, and SnCl_2 .

The representatives of the epoxy group-containing silicic compound expressed by the general formula (1) are the following.



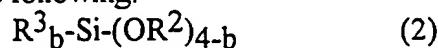
(In the formula, R^1 is an epoxy group-containing organic group, R^2 is an alkyl group of carbon number 1 ~ 5, and a is 1 ~ 3).

They are

β -glycidoxyethyltrimethoxysilane
 γ -glycidoxypropyltrimethoxysilane
 bis(glycidoxymethyl)dimethoxysilane
 tris(glycidoxy)methoxysilane
 3,4-epoxycyclohexylmethyltrimethoxysilane
 3,4-epoxycyclohexylmethyltriethoxysilane

etc. etc., and they include those of which a part or all of alkoxy groups are replaced by hydroxyl groups by the hydrolysis by the addition of the aqueous solution of hydrochloric acid, and also the condensate of the aforesaid hydroxyl groups.

The representatives of the silicic compound expressed by the general formula (2) are the following.



(In the formula, R^3 is an alkyl group of carbon number 1 ~ 6, vinyl group, methacryloxy group, mercapto group, or chlorine-containing organic group, and b is 0 ~ 3).

They are

methyltrimethoxysilane
 ethyltriethoxysilane
 vinyltriethoxysilane
 γ -methacryloxypropyltrimethoxysilane
 mercaptopropyltrimethoxysilane
 chloropropyltrimethoxysilane
 tetramethoxysilane
 tetraethoxysilane

etc. etc., and they include those of which a part or all of alkoxy groups are replaced by hydroxyl groups by the hydrolysis by the addition of the aqueous solution of hydrochloric acid, and also the condensate of the aforesaid hydroxyl groups. In case they are used without hydrolysis, the cured coat tends to be nonuniform, and sometimes the cured coat whitens.

As described in the foregoing, the aqueous solution of hydrochloric acid functions as the hydrolysis catalyst of alkoxy group, and preferably 0.01 ~ 0.5 N hydrochloric acid solution is added by 5 ~ 50 wt % of the weight of the silicic compound. Even if the treating liquid obtained here is coated and cured, the wear resistance of the coat is not enough. However, if the aforesaid amount of addition is further increased or the concentration of the hydrochloric acid is increased, the hydrochloric acid solution functions as the hydrolysis catalyst of alkoxy group and then as the ring opening catalyst of epoxy group, and the quality of the cured coat obtained is improved drastically, but the pot life of the treating liquid becomes extremely short. Consequently, by keeping the amount of addition of the hydrochloric acid solution low, and by using $SnCl_2$ which functions as the epoxy ring opening catalyst and crosslinking agent by small addition, it became possible that the pot life of the treating liquid is maintained long and yet the coat can be cured sufficiently at relatively low temperature in a short time, and its adhesion to the substrate material is good. The amount of addition of $SnCl_2$ is preferably 0.01 ~ 5 wt

% to the weight of the epoxy group-containing silicic compound, and if it is less than 0.01 wt %, the quality of the coat such as wear resistance, hot water durability, etc. is not sufficient, and if it exceeds 5 wt %, the pot life of the treating liquid becomes short.

As described in the foregoing, SnCl_2 functions not only as the epoxy ring opening catalyst, but also as the crosslinking agent, and this is the point which is different from other epoxy ring opening catalyst, and it contributes to densify the cured coat, and while maintaining the hardness, wear resistance, and hot water durability of the cured coat, it also contributes to keep the adhesion of the coat to the substrate material.

Although SnCl_4 functions similarly to SnCl_2 , it tends to shorten the pot life of the treating liquid. Also, the cured coat formed by the treating liquid, in which hydrochloric acid solution is not used and only SnCl_2 or aqueous solution of SnCl_2 is used as the catalyst and/or crosslinking agent, is poor in wear resistance in all cases, and also, in the case of combined use of the alkoxy group hydrolysis catalyst other than the hydrochloric acid solution and SnCl_2 , for example, in the case the hydrolysis catalyst of which the boiling point is higher than the baking temperature of the cured coat is used, the pot life of the treating liquid is short and in many cases the cured coat is discolored, and also the wear resistance of the cured coat is lower than in the case hydrochloric acid solution is used. On the other hand, when other volatile hydrolysis catalyst such as nitric acid, acetic acid, formic acid, etc. were used combined with SnCl_2 , the wear resistance of the cured coat was extremely low in all cases.

The solvent which can be contained in the treating liquid of the present invention is alcohol such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, etc., cellosolve such as methylcellosolve, ethylcellosolve, etc., ether, ester, carboxylic acid, halide, aromatic compound, ketone, etc., and these are used individually or as a mixture. Furthermore, in order to improve the appearance of the cured coat, surfactant (flow control agent) may be used as needed.

The coating method can be any of the known methods such as dipping method, spraying method, roll coater method, etc.. Also, the baking condition of the cured coat is at the temperature lower than the thermal deformation temperature of the substrate material, and usually $60^\circ\text{C} \sim 250^\circ\text{C}$, for 10 minutes \sim 4 hours. The thickness of the cured coat varies depending on the object but preferably it is $0.1 \sim 20 \mu\text{m}$.

Also, in the present treating liquid, various monomers or polymers which are compatible with the aforesaid silicic compound can be added. For example, they can be monomers or polymers of epoxy group-containing substance, acrylic group-containing substance, styrene group-containing substance, melamine-containing substance, or cellulose, etc., and they are used in the amount less than 100 wt % of the weight of the aforesaid silicic compound.

In the following, the present invention is explained further in detail by the examples, but the present invention is by no means limited by them. Parts and % show, respectively, parts by weight and weight %.

Also, the performance evaluation of the cured coat was carried out by the following methods.

(Wear resistance)

By rubbing with #000 steel wool, the condition of scratch was studied and judged by the following criteria.

- A. No scratch even by strong rubbing.
- B. A little scratch by strong rubbing.
- C. Scratched even by weak rubbing.

(Adhesion)

So-called cross cut adhesion test. 100 squares were cut at 1 mm spacing on the surface of the cured coat with a knife, and after sticking cellophane adhesive tape, the tape was peeled off, and the adhesion was indicated by the number of squares which do not peel off.

(Hot water durability)

By soaking in boiling water for an hour, the condition of the cured coat was studied.

(Heat resistance)

After holding the sample in the drying oven at 130°C for 100 hours, the condition of the cured coat was studied.

(Chemical durability)

After soaking the sample in 5 % sulfuric acid, 1 % sodium hydroxide, 95 % ethanol, acetone, toluene, and 1 N brine, respectively, at 40°C for 7 days, the condition of the cured coat was studied.

(Light resistance)

At the fade-o-meter 400 hours, the condition of the cured coat was studied.

Example 1

γ -glycidoxypolytrimethoxysilane 88.5 parts and tetramethoxysilane 57 parts were dissolved in isopropylalcohol 100 parts, and further, 0.05 N hydrochloric acid aqueous solution 47.7 parts was added, and the hydrolysis was carried out by stirring for 2 hours at room temperature, and subsequently, acetylacetone 30 parts was added, and digested for more than 20 hours at room temperature. SnCl_2 0.4 part and a small amount of flow control agent were added to this, and the mixture was stirred, and thus the treating liquid was prepared.

The treating liquid was coated on the cleaned CR-39 plate and acrylic plate by dipping method, and the former was baked at 130°C for 90 minutes and the latter at 80°C for 3 hours. The cured coat obtained was 3 μm thick and both of them were transparent, and the wear resistance was A, adhesion was 100/100, and also their hot water durability, heat resistance, chemical durability, and light resistance were good, and even after the hot water durability test, their wear resistance and adhesion were A and 100/100.

Furthermore, the aforesaid treating liquid was stored at room temperature, and it was coated on the CR-39 plate and acrylic plate after 10 days, 20 days, 30 days, and 40 days, and the quality was confirmed. No difference in quality was found on the sample of up to 30 days storage, and the sample of 40 days storage showed degradation of the wear resistance. That is, the pot life of the treating liquid was as long as a month, which is good.

Example 2

3,4-epoxycyclohexylmethyltrimethoxysilane 100 parts and tetraethoxysilane 65 parts were dissolved in isopropylalcohol 100 parts, and further, 0.05 N hydrochloric acid aqueous solution 49.5 parts was added, and after stirring for 2 hours at room temperature, digested for more than 20 hours. Subsequently, methanol 50 parts, isobutanol 50 parts,

SnCl_2 0.8 part, and a small amount of flow control agent were added, and thus the treating liquid was prepared.

The treating liquid was coated on the cleaned CR-39 plate by dipping method, and baked at 130°C for 2 hours. The cured coat obtained was $2.5\ \mu\text{m}$ thick and transparent, and the wear resistance was A, adhesion was 100/100, and its hot water durability, heat resistance, chemical durability, and light resistance were good, and even after the hot water durability test, its wear resistance and adhesion were A and 100/100.

Also, the pot life of the treating liquid was 2 months.

Comparison example 1

3 kinds of treating liquid were prepared by adding, respectively, ammonium perchlorate 0.07 part, 4 % benzene solution of aluminum acetylacetonate 15 parts, and SnCl_4 0.6 part in place of SnCl_2 in the preparation of the treating liquid in the example 1.

The treating liquid was coated on the cleaned CR-39 plate and the acrylic plate similarly to the example 1, and after baking, the quality of the cured coat was examined.

The cured coat obtained by using ammonium perchlorate discolored to brown, and the pot life of the treating liquid was as short as a week.

The cured coat obtained by using aluminum acetylacetonate showed B in wear resistance, and the adhesion to the substrate material was as poor as 30/100.

The quality of the cured coat obtained by using SnCl_4 was good, but the pot life of the treating liquid was as short as a week or so.

Comparison example 2

In the preparation of the treating liquid in the example 1, treating liquids were prepared by using 0.01 N nitric acid solution 50 parts, 0.02 N H_2SO_4 solution 50 parts, and 85 % formic acid 25 parts, respectively, in place of 0.05 N hydrochloric acid solution, and they were coated on the CR-39 plate and acrylic plate similarly to the example 1, and baked, and the quality of the cured coat was examined.

In all of the cured coats, the wear resistance was B and the adhesion was 50 ~ 70/100, which was not enough. Also, the cured coat obtained by using 0.02 N H_2SO_4 aqueous solution discolored to brown.

Although plastic was used as the substrate in the explanation of the examples, etc. in the foregoing, the present invention can be applied to other substrate such as wood, metal, etc..

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